

**NASA CONTRACTOR REPORT**

**THEORETICAL DETERMINATION OF CHEMICAL RATE CONSTANTS  
USING NOVEL TIME-DEPENDENT METHODS**

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**CONTRACT NAS2-**



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16. Abstract  <p><b>Abstract.</b> The work completed within the grant period 10/1/91 through 12/31/93 falls primarily in the area of reaction dynamics using both quantum and classical mechanical methodologies. Essentially four projects have been completed and have been or are in preparation of being published. The majority of time was spent in the determination of reaction rate coefficients in the area of hydrocarbon fuel combustion reactions which are relevant to NASA's High Speed Research Program (HSRP). These reaction coefficients are important in the design of novel jet engines with low NO<sub>x</sub> emissions, which through a series of catalytic reactions contribute to the deterioration of the earth's ozone layer. A second area of research studied concerned the control of chemical reactivity using ultrashort (femtosecond) laser pulses. Recent advances in pulsed-laser technologies have opened up a vast new field to be investigated both experimentally and theoretically. The photodissociation of molecules adsorbed on surfaces using novel time-independent quantum mechanical methods was a third project. And finally, using state-of-the-art, high level <i>ab initio</i> electronic structure methods in conjunction with accurate quantum dynamical methods, the rovibrational energy levels of a triatomic molecule with two nonhydrogen atoms (HCN) were calculated to unprecedented levels of agreement between theory and experiment.</p> <p style="text-align: right;">STAR-Category C-28</p>			
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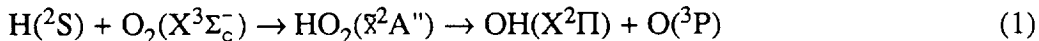
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## Introduction.

The work completed within the grant period 10/1/91 through 12/31/93 falls primarily in the area of reaction dynamics using both quantum and classical mechanical methodologies. Essentially four projects have been completed and have been or are in preparation of being published in the literature. The majority of time was spent in the determination of reaction rate coefficients in the area of hydrocarbon fuel combustion reactions which are relevant to NASA's High Speed Research Program (HSRP). These reaction coefficients are important in the design of novel jet engines with low NO<sub>x</sub> emissions, which through a series of catalytic reactions contribute to the deterioration of the earth's ozone layer. A second area of research studied concerned the control of chemical reactivity using ultrashort (femtosecond) laser pulses. Recent advances in pulsed-laser technologies have opened up a vast new field to be investigated both experimentally and theoretically. The photodissociation of molecules adsorbed on surfaces using novel time-independent quantum mechanical methods was a third project. And finally, using state-of-the-art, high level *ab initio* electronic structure methods in conjunction with accurate quantum dynamical methods, the rovibrational energy levels of a triatomic molecule with two nonhydrogen atoms (HCN) were calculated to unprecedented levels of agreement between theory and experiment.

### The HO<sub>2</sub> system.

The reaction between ground state hydrogen atoms and molecular oxygen,

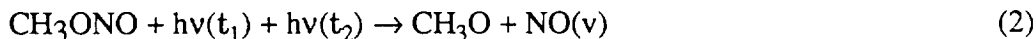


is one of the most important elementary reactions in gas phase combustion and occurs in the oxidation mechanism of all hydrocarbons. In addition, the HO<sub>2</sub> radical is an important intermediate for many chemical reactions such as those involved in atmospheric chemistry, stratospheric formation and destruction of ozone, and photochemical air pollution.

Work has been completed on the HO<sub>2</sub> system. The *ab initio* CASSCF/CI data of Walch and coworkers<sup>1</sup> has been fit to a compact analytic form to describe the global surface including a proper description of the long-range intermolecular forces. This work is being written in a paper to be submitted for publication shortly[1]. In addition, quasiclassical trajectory studies have been run to obtain the rate coefficients for the forwards and reverse reactions in Eq. (1) at combustion temperatures ranging from 2000 to 5000 K. The manuscript for this work is also in preparation[2].

### Vibrational Predissociation of CH<sub>3</sub>ONO.

In collaboration with Professor H. Metiu at UC Santa Barbara, we have studied the vibrational predissociation of methylnitrite using phase-locked ultra-short laser pulses using novel time-dependent wave-packet methods based on fast Fourier Transforms. Using a two-dimensional model potential, the time-dependent Schrödinger equation is solved numerically to study the reaction



The two pulses are identical except for their relative phase (*i.e.*, the time at the peak intensity of the laser pulse). Because the wave functions (or population amplitudes) created by each individual pulse can interfere, the total product population created by the joint action of the two pulses differs from that created by two independent laser pulses.

Both the NO total yield and the vibrational populations are found to oscillate with the delay time  $\Delta t = (t_2 - t_1)$ , with a period corresponding to the off-resonance frequencies

(the difference between the laser pulse central frequency and the excited state vibrational levels). Hence, we suggest a type of experiment which provides a means of using quantum interference for a modest control of photodissociation. This work already has been published[3].

### **Photodissociation of Surface Adsorbed Molecules**

The interaction between photons and molecules adsorbed on surfaces is fundamentally and practically important for surface science. The photodissociation of an adsorbate contains potentially a wealth of valuable information regarding the orientation, the alignment, and the existence of ordering of the adsorbates, the substrate-adsorbate interaction potential, and in some cases also the surface structure. The study of photodissociation reactions of adsorbates is thus of importance for understanding and hence optimizing processes such as laser induced surface processing, heterogeneous catalysis and film growth.

Using a time-independent quantum mechanical model, we studied the photodissociation of  $\text{HBr}/\text{LiF}(001)$ , a system of considerable experimental interest which exhibits clear quantal effects. The photodissociation lineshape, the  $\text{Br}(^2\text{P}_{1/2})/\text{Br}(^2\text{P}_{3/2})$  yield ratio, and the angular distribution of the photofragments are computed, and the effect of polarization of the light field is illustrated and discussed. Qualitative agreement with experiment is found. This work has been published[4].

### **An *ab initio* potential for HCN/HNC isomerization and vibrational analysis**

In collaboration with Dr. T.J. Lee of NASA Ames and Professor J. Bowman and his research group at Emory University we have determined a new and accurate *ab initio* potential for the HCN/HNC isomerization. The highly accurate CCSD(T) coupled-cluster method in conjunction with large atomic natural orbital basis set was used to generate over 1200 points which were fitted to a bicubic spline-Morse potential. Exact vibrational calculations were performed using a truncation/recoupling scheme in a finite basis representation procedure with a moveable basis. The properties of this potential and vibrational calculations are compared to experiment. The level of agreement with experiment is unprecedented for a triatomic molecule with two non-hydrogen atoms. In addition, a simulation of the  $(\tilde{A}-\bar{x})$  stimulated emission spectrum (SEP) is calculated and compared to all available experimental data. The present surface, which is based solely on unadjusted *ab initio* data appears to be capable of yielding vibrational states up to very high energies to within  $10\text{-}40\text{ cm}^{-1}$  of experiment. In the course of these studies we have also determined quartic force fields for both HCN and HNC from which accurate spectroscopic constants may be derived in order to aid in the interpretation of future high-resolution, rovibrational studies of HNC. This work has been published[5-7].

**Publications published and in preparation under Cooperative Agreement NCC2-737**

1. C.E. Dateo, "*A New Global Potential Energy Surface for the Hydroperoxyl Radical*," in preparation.
2. C.E. Dateo, "*Reaction Rate Coefficients for  $H+O_2 + O+OH$  at Combustion Temperatures (1000-5000 K)*," in preparation.
3. C.E. Dateo and H. Metiu, "*Vibrational Predissociation of Methylnitrite Using Phase-Locked Ultrashort Laser Pulses*," *Journal of Chemical Physics* **98**, 1957 (1993).
4. T. Seideman, "*Photodissociation Dynamics of  $HBr/LiF(001)$ : A Quantum Mechanical Model*," *Journal of Chemical Physics* **99**, 4766 (1993).
5. J.A. Bentley, J.M. Bowman, B. Gazdy, T.J. Lee, and C.E. Dateo, "*A Global Ab Initio Potential for HCN/HNC, Exact Vibrational Energies, and Comparison to Experiment*," *Chemical Physics Letters* **198**, 563 (1992).
6. B. Gazdy, J.A. Bentley, J.M. Bowman, C.E. Dateo, and T.J. Lee, "*Exact Calculations of Vibrational Properties of HCN/HNC Using a Global Ab Initio Potential Surface, and a Simulation of the Stimulated Emission Pumping Spectrum*," *Journal of Chemical Physics* **98**, 308 (1993).
7. T.J. Lee, C.E. Dateo, B. Gazdy, and J.M. Bowman, "*Accurate Quartic Force Fields and Vibrational Frequencies fo HCN and HNC*," *The Journal of Physical Chemistry*. **97**, 8937 (1993).